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Conducting an evaluation of CBRN canister protection capabilities against emerging chemical and radiological hazards

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ABSTRACT

In the event of a chemical, biological, radiological, or nuclear (CBRN) hazard release, emergency responders rely on respiratory protection to prevent inhalation of these hazards. The National Institute for Occupational Safety and Health's (NIOSH) CBRN Statement of Standard calls for CBRN respirator canisters to be challenged with 11 different chemical test representative agents (TRAs) during certification testing, which represent hazards from 7 distinct Chemical Families; these 11 TRAs were identified during the original 2001 CBRN hazard assessment. CBRN hazards are constantly evolving in type, intent of use, and ways of dissemination. Thus, new and emerging hazards must be identified to ensure CBRN canisters continue to provide protection to emergency responders against all hazards that would most likely be used in an intentional or unintentional event.

The objectives are to: (1) update the CBRN list of hazards to ensure NIOSH-approved CBRN canisters continue to provide adequate protection capabilities from newly emerging chemical and radiological hazards and (2) identify the need to update NIOSH TRAs to ensure testing conditions represent relevant hazards. These objectives were accomplished by reviewing recent hazard assessments to identify a list of chemical and radiological respiratory hazards, evaluate chemical/physical properties and filtration behavior for these hazards, group the hazards based on NIOSH's current Chemical Families, and finally compare the hazards to the current TRAs based on anticipated filtration behavior, among other criteria.

Upon completion of the evaluation process, 237 hazards were identified and compared to NIOSH's current CBRN TRAs. Of these 237 hazards, 203 were able to be categorized into one of NIOSH's current seven Chemical Families. Five were identified for further evaluation. Based on reviewing key chemical/physical properties of each hazard, NIOSH's current 11 TRAs remain representative of the identified respiratory CBRN hazards to emergency responders and should continue to be used during NIOSH certification testing. Thus, NIOSH's CBRN Statement of Standard remains unchanged. The process developed standardizes a methodology for future hazard evaluations.

KEYWORDS
Carbon filtration; personal protective equipment; respirator; test representative agent

Introduction

The National Institute for Occupational Safety and Health (NIOSH) is the federally mandated agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness (DHHS 1995). Among its many responsibilities, NIOSH houses the Respirator Approval Program where its primary functions include developing and implementing respirator performance standards used in occupational settings, and approving respirators by ensuring they meet minimum performance requirements. In 2003, NIOSH and its federal partners developed the Statement of Standard for chemical, biological, radiological, and nuclear (CBRN) full-facepiece air-purifying respirators (APRs) (NIOSH 2005). The Statement of Standard establishes performance and design requirements for APRs used by U.S. emergency responders (NIOSH 2005; 2018). In 2001, during the initial phases of

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Table 1. Summary of filtration performance characteristics based on vapor pressure (adapted from Karwacki and Jones 2000).

Effective Filtration Performance	Marginal Filtration Performance	Poor Filtration Performance
• Generally, chemicals with a VP less than 10 mmHg at 25 °C • Strong adsorption to the activated carbon • Desorption unlikely but enhanced by high %RH if a chemical is immiscible with water	• Generally, chemicals with a VP between 10–100 mmHg at 25 °C • Moderate adsorption to the activated carbon • Desorption likely to occur and enhanced by high %RH if a chemical is immiscible with water • Chemisorption may be necessary for adequate filtration	• Generally, chemicals with a VP greater than 100 mmHg at 25 °C • Weak adsorption to the activated carbon • Desorption will occur and enhanced by high %RH if a chemical is immiscible with water • Chemisorption is required for adequate filtration

development of the standard, a CBRN hazard assessment was conducted where all potential CBRN hazards likely to be used in an intentional or unintentional disaster relevant to emergency responders were compiled and evaluated (U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) 2003; DHHS 2001; Thornton 2001; DHHS 2000). This hazard assessment concluded with identifying 139 CBRN hazards (referred to as the 2001 NIOSH CBRN APR Canister Protection List), where all NIOSH-approved CBRN APR canisters provide protection against a minimum of these 139 identified CBRN hazards. These hazards were categorized into NIOSH's seven current Chemical Families (NIOSH 2005). These Chemical Families share common chemical properties and filtration behavior (NIOSH 2018). To reduce the number of laboratory tests required to evaluate CBRN canisters used with APRs, NIOSH challenges the canisters using 11 different test representative agents (TRAs) spanning 7 Chemical Families (NIOSH 2018). TRA selection considerations include chemical/physical properties (e.g., vapor pressure [VP], flammability, stability) chemical cost, detectability, ease of handling, ability to safely generate as a challenge mixture with air, toxicity, and effect of adsorbed moisture on the carbon bed (Smith 1996). The original 139 CBRN hazards identified in 2001 remain as the current NIOSH CBRN APR Canister Protection List, and the 11 original TRAs are still currently used for NIOSH approval of CBRN APRs.

APR CBRN canisters use a combination of materials to filter out respiratory hazards. Fibrous media is generally used to remove solid and liquid aerosols, while activated carbon is used to remove gaseous and vaporous components (DeCoste and Peterson 2014). Activated carbon-based filters have been used for decades to protect military and emergency responders from hazardous chemical agents (Lodewyckx and Verhoeven 2003). Filtration of chemicals by the CBRN canister (comprising of activated carbon and a HEPA/P100 filter) is done by various mechanisms, primarily physical adsorption, mechanical capture, and chemisorption/chemical reaction. Approximations of a canister's chemical removal performance may be made using chemical/physical properties, with an emphasis on VP (Table 1, adapted from Karwacki and Jones 2000). Many chemicals with VP lower than 100 millimeters of mercury (mmHg) (e.g., nerve agents) primarily undergo strong and irreversible physical adsorption onto the activated carbon and is largely governed by Van der Waals forces—interactions are largely dependent on physical properties (e.g., VP) of the chemical and the activated carbon (Karwacki and Jones 2000). Cyclohexane's VP (100 mmHg at 25 °C) is generally used in practice as the cutoff for chemicals that physically adsorb well to activated carbon without requiring utilization of covalent electronic interactions for adequate removal (e.g., catalysis, chemisorption) (Karwacki and Jones 2000; NIOSH 2018; National Center for Biotechnology Information 2020). Chemicals with vapor pressures between 10 and 100 mmHg will generally be physically adsorbed, but the effect of adsorbed water and risk of desorption is greater than those chemicals below 10 mmHg (Karwacki and Jones 2000).

Particulates and chemicals with very low vapor pressure will primarily undergo mechanical filtration—i.e., the collection of particles in a filter by diffusion, impaction, interception, and electrostatic by the HEPA/P100 filter within the canister. The HEPA/P100 filter filters 99.97% of particulates of 0.3 microns diameter aerosol particles. Mechanical and physical adsorption filtration mechanisms are typically nonselective, thus allowing predictions of filtration behavior based on particle size (mechanical filtration) and a chemical's VP and other physical/chemical properties (physical adsorption).

Chemicals with weak intermolecular forces typically have weak physical adsorption to the carbon surface and require complex chemical reactions for adequate removal (DeCoste and Peterson 2014). Chemicals with high VP (e.g., greater than 100 mmHg) often require unique chemisorption/chemical reactions with different moieties (i.e., impregnants) within the activated carbon for adequate filtration. These impregnants typically include metal salts, acids, and amines (DeCoste

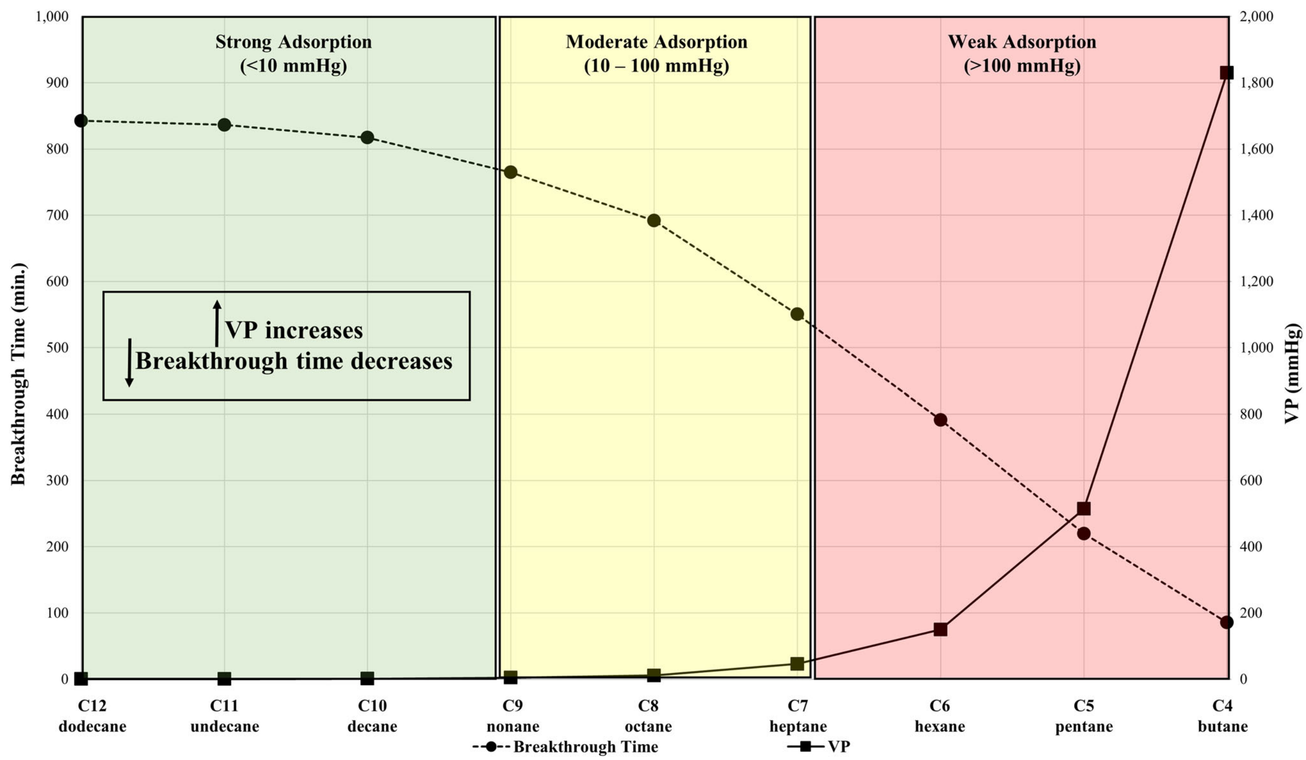

Figure 1. Example of applying the Mecklenburg equation to model the breakthrough time of nine hydrocarbons based on VP.

and Peterson 2014). Chemisorption/chemical reactions involve the covalent interactions and explicit electron transfer between the toxic chemical and the impregnated metal oxides, which improves filtration performance (Jonas 1978; Bansal and Goyal 2005).

There are numerous models developed to predict activated carbon filtration data that are appropriate for chemicals that primarily undergo physical adsorption, including the Wheeler and Jonas model (Wheeler and Robell 1969; Jonas and Rehrmann 1973) and Mecklenburg model (Mecklenburg 1930). Figure 1 shows an example of applying the predictive Mecklenburg model equations using a series of hydrocarbons (removed via physical adsorption) on impregnated activated carbon typically used for commercial CBRN canisters. The three VP categories used to predict filtration behavior (i.e., <10 mmHg [irreversibly-adsorbed], 10–100 mmHg [moderately-absorbed], >100 mmHg [weakly adsorbed]) are depicted. Below 10 mmHg, predicted breakthrough times generally plateau. Between 10–100 mmHg, capacity is still observed but to a lesser extent and breakthrough times begin to shorten, and above 100 mmHg, breakthrough times more rapidly declines. Cyclohexane (NIOSH's OV TRA) is at the high end of the moderate adsorption category and is informally viewed as a halfway filtration performance point between those OV chemicals that strongly adsorb to carbon (e.g., dodecane) and those that weakly adsorb (e.g., butane, carbon monoxide). It is not always straightforward to determine how or if a chemical will be adequately filtered based solely on VP. Service-life estimates for reactive chemicals rely largely on empirical data due to the complex nature of adsorptive reactions (Karwacki and Jones 2000; Wood 2005).

These filtration principles were used by NIOSH and its federal partners during the 2001 hazard assessment for the selection of the TRAs and NIOSH's current CBRN APR Protection List (NIOSH 2005). By leveraging these principles, an updated CBRN APR Canister Protection List (herein referred to as the CBRN List) and thorough evaluation of TRAs is necessary to ensure NIOSH's current TRAs still accurately represent emerging chemical and radiological hazards. Since the initial hazard assessment conducted in 2001, additional traditional and nontraditional chemical hazards have emerged, and methods of deployment and dissemination have changed (USACHPPM 2003). Furthermore, new research and laboratory data have become available to verify the selection of current TRAs and update NIOSH's CBRN List.

The primary objectives of this effort were to (1) review recent chemical hazard assessments to identify new and emerging chemical and radiological hazards and (2) develop an evaluation process to determine

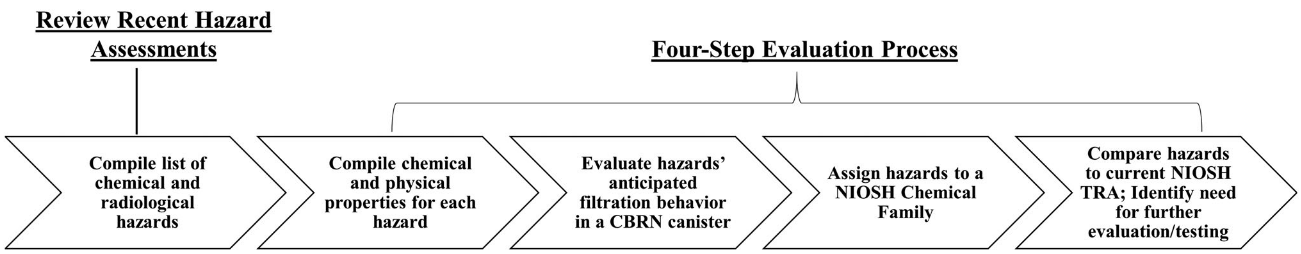

Figure 2. Summary of the four-step evaluation process.

the need for updating NIOSH's current CBRN TRAs to reflect these newly identified hazards. The primary focus while generating this updated CBRN List was chemical gas/vapors, chemical particulates, and radiological particulate hazards. Biological hazards were not included in this evaluation, partially because these hazards do not carry the same complexity of filtration mechanisms as gas/vapor chemical hazards and would primarily be removed by the HEPA/P100 filter within the CBRN canisters (Yamamoto and Eninger 2018).

Methods

Summary of process

NIOSH collaborated with the Department of Defense Combat Capabilities Development Command Chemical Biological Center (DOD CCDC CBC), the DOD-Naval Research Laboratory (NRL), and the Department of Homeland Security Science and Technology Directorate Chemical Security Analysis Center (DHS S&T CSAC) to identify and evaluate emerging chemical and radiological hazards against NIOSH's current TRAs. First, recently conducted chemical hazard assessments were reviewed to identify emerging respiratory hazards relevant to emergency responders. Second, a four-step evaluation process was developed to systematically assess the newly identified hazards; the process was documented in such a way that it can be used for future evaluations. Figure 2 shows a summary of the steps taken to complete this evaluation process. The components of this process were largely based on the steps taken during the original 2001 evaluation process (not formally published).

Identify hazards by reviewing recent chemical hazard assessments

The primary focus while generating this updated CBRN List was chemical gas/vapors, chemical particulates, and radiological particulate hazards. To generate the updated CBRN List, five recent risk-based chemical assessments performed by the DOD and DHS were reviewed. These risk-based assessments generally included chemicals that pose risk to military personnel and/or to public health from an intentional or accidental chemical release based on its likelihood of use and potential severity of negative health effects resulting from exposure. Each of the assessments included an evaluation of risk considering factors that would influence the likelihood that a chemical would be used and the potential consequences of its use. These assessments included:

- International Task Force (ITF)-40 Report (USACHPPM 2003)—developed for military commanders to identify, assess, and control exposures to industrial chemicals in military situations. Risk is evaluated by assessing the severity of the hazard and probability of exposure. The 33 chemicals identified on the "toxic inhalation hazard list" were considered for this current study.
- CSAC Screening Assessment (Paulus et al. 2007)—developed to have a comprehensive list of chemicals that have the highest potential risk to the U.S. homeland. Evaluated risk-based on the likelihood and consequence of a potential attack. Chemicals were ranked from "low risk" to "extreme risk." A total of 142 extreme or high-risk chemicals were recommended for further evaluation. This list of 142 chemicals was considered for the current study.
- NRL Industrial Chemical Analysis Evaluation of Inhalation/Ocular Hazards of Industrial Chemicals (Sutto 2011)—developed to assess the potential hazards of industrial chemicals to the warfighters. Evaluated risk by assessing toxic hazard and probability of use. Stability of the chemical in an operational environment was also evaluated by accounting for potential chemical reactions or combustion processes. The resulting 49 critical inhalation/ocular hazard chemicals were considered for the current study.
- CSAC's Chemical Terrorism Risk Assessment (CTRA) (Brevett et al. 2017a; 2017b; 2017c; 2018a; 2018b)—developed to assess chemical terrorism

risk related to industrial chemicals, chemical warfare agents, pharmaceuticals, and nontraditional agents. This assessment is a recurring effort that updates the threat profile based on information from the intelligence and law enforcement communities regarding the likelihood of a given attack scenario. The CTRA evaluates risk based on the probability of a given attack and the consequences of the attack and identifies hazards based on their fatality and/or public health risk. The 184 chemicals on the current CTRA list were considered for the current study. These chemicals were considered most relevant for this study based on an algorithmic effort assessing both probability and severity of potential exposure.

- NRL conducted a review and assessment of potential radiological hazards based on radiological elements of concern for different scenarios—i.e., radioactive isotypes typically used in a medical or industrial setting, nuclear power plant, and detonation of a nuclear device. This assessment was done in 2017 but unpublished. The 46 potential radiological hazards from this list were considered for the current study.

The CTRA was the most recent hazard assessment and included the most extensive chemical list, including emerging threats. For these reasons, it was the foundation of the updated CBRN List. Chemicals from the NRL Critical Inhalation/Ocular Hazards List and the ITF-40 list of inhalation hazards were added to this list.

Evaluation process, Step 1: Collect chemical and physical properties for each hazard

The first evaluation step involved an assessment of the chemical and physical properties for each hazard on the updated CBRN List. Properties of interest included the primary state of the hazards at ambient conditions (e.g., solid particulate/aerosol, liquid, liquid-vapors, or gas) and VP, though many other properties were recorded. VP was important to determine how well a gas/vapor would physically adsorb to the carbon and be sufficiently removed by the CBRN canister. After collecting these properties, the hazards were categorized into groupings based on the state of the hazard at ambient conditions (i.e., those that exist as solid particulate/aerosols and those that exist as gases or vapors). Because physical adsorption is considered the essential first step for the removal of a chemical which is heavily influenced by VP (Jonas 1978), the VP of each chemical was used as the primary criterion.

For liquids, gases, and vapors, hazards were further categorized into four VP groupings to use when evaluating the anticipated filtration behavior (Step 2): (1) ≤ 10 mmHg; (2) > 10 to ≤ 100 mmHg; (3) > 100 mmHg; and (4) gases (Karwacki and Jones 2000; Peterson and Karwacki 2007). These groupings were also used during the 2001 hazard assessment (Edgewood Chemical Biological Center (ECBC) 2001; Karwacki and Jones 2000) and relate to the VP thresholds to undergo the three primary filtration mechanisms identified in Step 2. Because the focus of this evaluation was to identify candidate NIOSH TRAs for use during laboratory evaluation of CBRN APR canisters, hazards considered to be unstable were removed during this step of the evaluation process. Unstable hazards included those that spontaneously decompose and react with water vapor in air, spontaneously ignite in air, rapidly polymerize in air, and/or degrade quickly; these characteristics are not suitable for a laboratory TRA, as reproducibility, safety, and representativeness of the chemical family are key criteria.

Evaluation process, Step 2: Evaluate anticipated filtration behavior

Using the chemical and physical property data compiled from Step 1, hazards were then categorized based on their anticipated or known filtration behavior. Determining the anticipated filtration mechanism is important as it allows for proper grouping of each hazard into the appropriate NIOSH Chemical Families (Step 3), further allowing each hazard to be compared to the current TRA in the chemical family to determine if the current TRA within each family remains representative.

The chemicals were categorized based on the three main filtration mechanisms previously described: (1) mechanical capture (by the HEPA/P100 filter); (2) physical adsorption to the activated carbon; or (3) through chemical reaction/chemisorption with impregnants in the carbon bed. Chemicals occurring in particulate form and vapors with low VP (i.e., < 10 mmHg) were considered to primarily undergo mechanical filtration and physical adsorption, respectively. Chemicals with VP between approximately 10–100 mmHg were considered to primarily undergo physical adsorption filtration, where chemicals with VP greater than 100 mmHg were considered to primarily require chemical reaction/chemisorption for sufficient removal (Karwacki and Jones 2000).

Understanding the filtration behavior for chemicals that undergo chemical reaction with the carbon and impregnants is highly dependent on measured filtration data. Therefore, an extensive data gathering review of 37 "For Official Use Only (FOUO)" technical reports was conducted, and a comprehensive database of filtration performance data was established. The FOUO reports were primarily used over publicly available reports as the FOUO reports describe explicit—and generally consistent—testing parameters (e.g., flow rate, relative humidity, carbon bed depth, carbon bed type, challenge concentration) which is generally not publicly available due to proprietary information of the carbon type. References for these can be found in the Supplemental Information. The objective of this compilation was to identify predictive performance trends for as many chemicals as possible for use during the evaluation. Specific parameters recorded included filter and carbon tube configurations, carbon mesh sizes, residence times, carbon bed depths, test flow rates, flow profiles, preconditioning and testing conditions, and challenge concentrations. Although this information was for filtration performance using military individual protection filters, the type of activated carbon used is similar to that used in commercial filters (e.g., similar physical properties of the activated carbon and similar impregnants). The filtration performance data compiled was used to evaluate potential modifications to NIOSH's existing TRAs.

Evaluation process, Step 3: Assign each hazard to a NIOSH chemical family

Next, the hazards were categorized into one of NIOSH's current seven Chemical Families to compare each chemical to the family's TRA. These families are primarily grouped based on the predominant mechanism by which a chemical is filtered by the carbon bed. The NIOSH Chemical Families include the Organic Vapor (OV) Family (physical adsorption), Acid Gas Family (chemisorption/chemical reactions), Base Gas Family (physical adsorption and chemisorption/chemical reactions), Formaldehyde Family (chemisorption/chemical reactions), Hydride Family (chemisorption/chemical reactions), Nitrogen Oxides Family (chemisorption/chemical reactions), and the Particulate Family (mechanical capture).

Chemicals that are primarily removed by the activated carbon through physical adsorption were grouped in the OV Family. Thus, it is generally straightforward to compare a chemicals' adsorption capacity based on VP. Alternatively, chemicals that undergo chemisorption are much less predictable due to the chemical-specific reactivity. Chemicals that exhibit the chemical reactivity of an acid (e.g., undergo acid-base reactions with the surface of the filtration media) or produce acidic byproducts were categorized in the Acid Gas Family. Similarly, chemicals that exhibit the chemical reactivity of a base or produce basic byproducts were categorized in the Base Gas Family. Base gases are removed primarily by physical adsorption, and secondarily through chemisorption (i.e., reported to form metal-amine complexes within the carbon bed) (Bansal and Goyal 2005; Karwacki et al. 2005; Jeguirim et al. 2018). Gases in the Nitrogen Oxides Family are highly reactive and require special considerations due to their unique chemistry. These gases are primarily removed via reduction. Chemicals with a chemical structure of XH_n with similar electronegativity generally must be catalytically removed via oxidation and were classified in the Hydride Family (Doughty 1991; Seredych et al. 2010). Although these chemicals are typically acid gases, they generally undergo different chemical reactions than acid gases and have unique properties that typically involve oxidation and reduction steps that affect the ability of the adsorbent to filter them. For example, ammonia is not included with the other hydrides such as arsine and phosphine due to significant differences in the donation of electron densities which affect their binding strength with metal centers (Bobbitt and Snurr 2017). Chemicals that self-polymerize were categorized in a group titled the Formaldehyde Family. Lastly, chemicals with very low VP that could be filtered out as a solid particulate/aerosol were categorized in the Particulate Family. This would include most radiological particulates that readily undergo a chemical reaction and/or combine with water to generate larger particle sizes (e.g., 400 nm – 100+ μm), which would be removed by the HEPA/P100 filter during mechanical capture (Dietchman 2001; Lee et al. 2010).

Hazards not easily assigned to an existing NIOSH Chemical Family were identified. Without measured experimental data, historical, or personal experience with these chemicals, it was difficult to categorize some chemicals into a NIOSH Chemical Family. These chemicals were individually considered and recorded for future filtration performance evaluation in the laboratory.

Evaluation process, Step 4: Compare to the current NIOSH TRA and identify need for testing

Once chemicals were categorized into a NIOSH Chemical Family, the information collected during Steps 1–3 was used to compare the chemical to the respective current TRA to determine if the current TRA was still representative of the Family. This evaluation and determination primarily considered empirical chemical and physical properties to appropriately represent the Chemical Family by constituting performance-limiting characteristics (e.g., low filtration performance). Other factors of consideration included candidate TRA parameters, including a hazard's toxicity, cost, availability, environmental effects, stability, and detectability (Moyer et al. 2001). Though all these criteria were under consideration if needed, the focus was primarily on VP and filtration performance in the carbon bed.

Results

Identify hazards by reviewing recent chemical hazard assessments

From the 5 chemical hazard assessment reports, a total of 237 hazards were identified, which included 191 unclassified chemicals and 46 radiologicals. This updated CBRN List includes traditional (e.g., toxic industrial chemicals [TICs]) and nontraditional chemicals (e.g., fentanyl). Thirty-six of the 237 chemicals were previously identified in the original 2001 NIOSH hazard assessment as part of NIOSH's CBRN APR Protection List (NIOSH 2005). An additional 14 classified chemicals—i.e., those chemicals that are restricted to personnel with necessary security clearance—were identified that will not be discussed in this paper.

Evaluation process, Step 1: Collect chemical and physical properties for each hazard

The hazards were then categorized into the broad physical property groupings, primarily based on VP. This concluded with 100 solids (chemical and radiological) and 137 gas/vapor chemicals, further categorized into 35 liquids with VP less than 10 mmHg, 45 liquids with VP from 10–100 mmHg, 22 liquids with VP greater than 100 mmHg, and 35 gases. Twenty-nine unstable chemicals were removed as candidate TRAs, leaving 208 candidate TRAs from the original 237. These unstable hazards included those that would rapidly break down to generate other hazards already identified on the list (e.g., boron trichloride breaking down and titanium tetrachloride to react with moist air to both generate hydrogen chloride). Of the radiologicals, 44 would primarily be encountered in the particulate form, where two would be encountered as a gas/vapor (i.e., radioactive iodine and radioactive methyl iodine).

Evaluation process, Step 2: Evaluate anticipated filtration behavior

Based on the hazards' state at ambient conditions and particle size, hazards identified as solid particulates (n = 56) and radiological particulates (n = 42) were determined to be removed by the HEPA/P100 filter and categorized in the mechanical filtration category. Based on chemical/physical properties and existing filtration data, 66 gas and vapor chemicals were identified as being primarily removed through physical adsorption, while 39 chemicals were determined to be primarily removed through chemical reaction/chemisorption. The filtration performance data compiled from the FOUO reports were used to compare the candidate TRAs to NIOSH's current TRAs, especially for those chemicals that require chemisorption and predictions of reactivity were difficult. It was not possible to identify a filtration mechanism for five gas/vapor chemicals, so these were determined to require further evaluation. Thus, 203 candidate TRAs were available at the end of Step 2 for evaluation to the current TRAs.

Evaluation process, Step 3: Assign each hazard to a NIOSH chemical family

Excluding 29 unstable chemicals identified in Steps 1 and 5 chemicals identified in Step 2 for further evaluation, 203 chemicals could be assigned to NIOSH's current Chemical Families based on their anticipated behavior in a carbon bed. Table 2 provides a summary of the hazards in the updated CBRN List and the current NIOSH CBRN APR Canister Protection List (NIOSH 2005). The 203 chemicals were categorized into the 7 Chemical Families as summarized below.

The hazards categorized into the OV Family are shown in Table S1 (Supplemental Information). A total of 66 hazards were categorized into NIOSH's OV Chemical Family based on available empirical chemical/property data and filtration data, particularly on the hazards that would be filtered primarily by physical adsorption. VP was the primary criterion to consider when categorizing OV chemicals, which was also

Table 2. Comparison between the hazards identified in the 2001 and 2018 CBRN Lists.

NIOSH Chemical Family *(current NIOSH CBRN TRA[s])*		Hazards in NIOSH's current CBRN APR Canister Protection List	Hazards in the updated CBRN List	Number of Repeated Hazards between Lists
OV (*cyclohexane*)		61	66	16
Acid Gas (*cyanogen chloride, hydrogen cyanide, hydrogen sulfide, phosgene, sulfur dioxide*)		32	29	10
Base Gas (*ammonia*)		4	4	2
Formaldehyde (*formaldehyde*)		1	1	1
Nitrogen Oxides (*nitrogen dioxide*)		5	3	2
Hydride (*phosphine*)		4	2	2
Particulate	**Chemical**	16	56	3
(*dioctyl phthalate*)	**Radiological**	16	42	11
Total		139	203	
Chemicals unable to be categorized		–	5	

used during the original hazard assessment (NIOSH 2018). The vapor pressures for these 66 hazards span a ~7 log range.

The hazards categorized into the Acid Gas Family are shown in Table S2. Twenty-seven hazards were categorized into this chemical family, as their vapors form acidic solutions when dissolved in water and require chemisorption to be effectively filtered in the carbon bed.

The hazards categorized into the Base Gas Family were ammonia (NIOSH's current TRA), dimethylamine, methylamine, and methyl hydrazine. These vapors form basic solutions when dissolved in water and require chemisorption to be effectively filtered in the carbon bed.

The hazards categorized into the Hydride Family were arsine and phosphine (NIOSH's current TRA). These gases were categorized into this family as they have hydrogen atoms bonded to an element of similar electronegativity, and are primarily removed via oxidation on impregnated activated carbon.

The hazards categorized into the Nitrogen Oxides Family were nitric acid, nitric oxide, and nitrogen dioxide (NIOSH's current TRA). These gases were categorized into this family as they are highly reactive and are primarily removed via reduction on impregnated activated carbon.

The only hazard categorized into the Formaldehyde Family was formaldehyde (NIOSH's current TRA). Formaldehyde undergoes self-polymerization in the filter media.

The hazards categorized into the Particulate Chemical Family are shown in Table S3. Fifty-six hazards were categorized into this chemical family, as they undergo mechanical filtration. As one example, fentanyl and its analogs were identified as they pose a risk of exposure to emergency responders as a result of the recent increase in illicit opioids and overdoses.

Forty-four radiological particulates were identified (Table S4). Two radiologicals (and their isotopes) were categorized into the Acid Gas Chemical Family due to the inherent gas/vapor hazard: radioactive iodine (131) and radioactive methyl iodide (133/131). These two chemicals typically dissociate and form acids (e.g., methyl iodide binds with amines or metal oxides within the carbon bed to dissociate and form hydrogen iodide).

Evaluation process, Step 4: Compare to the current NIOSH TRA and identify need for testing

Each chemical was compared to the current TRA in the respective NIOSH Chemical Family. Filtration performance data was leveraged from the FOUO reports, especially for those chemicals that require chemical reaction/chemisorption. It was determined that no identified hazard was considered a more suitable candidate TRA than NIOSH's current 11 TRAs which represent 7 families. Thus, no changes to NIOSH's CBRN TRAs or Chemical Families are needed at this time. A synopsis for each Chemical Family is below.

OV family

The 66 hazards identified in the OV Family are shown in Figure 3. Additionally, Figure 3 shows the general VP filtration performance categorization, where the VP categories that are not appropriate for a candidate TRA (i.e., VP too low or too high) is depicted. Cyclohexane's VP (i.e., 100 mmHg at 25 °C) is in the upper range of chemicals that are likely to be removed by activated carbon filters predominantly by physical adsorption (Karwacki and Jones 2000). Chemicals with a lower VP than cyclohexane are well represented by cyclohexane, as they would be better physically adsorbed to the activated carbon than cyclohexane (NIOSH 2018). Thus, cyclohexane remains representative of both the current and newly identified hazards in the OV Family. Cyclohexane represents performance-limiting characteristics and offers other advantages of a TRA over chemicals with similar filtration performance. For example, carbon

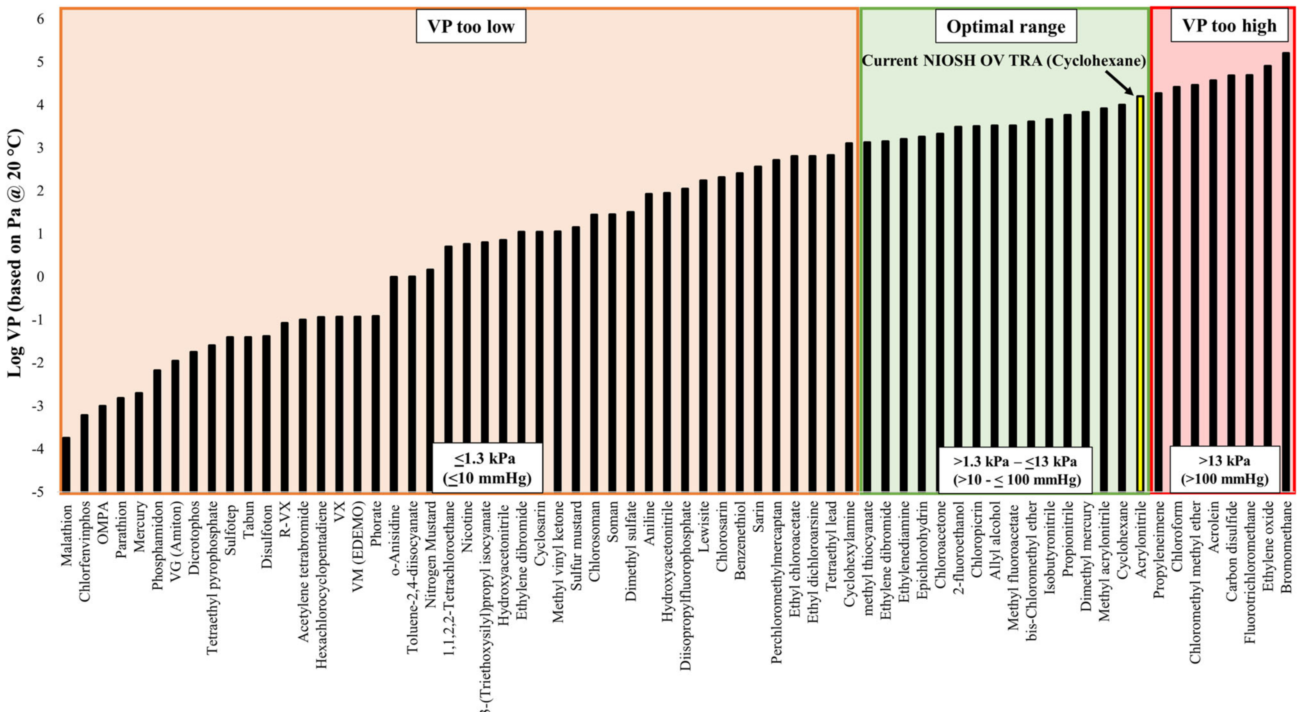

Figure 3. Plot of Log VP of selected chemicals in the Organic Vapor Family. Current NIOSH CBRN OV TRA is highlighted.

tetrachloride and cyclohexane are both easily detectable and behave similarly in the carbon bed, but carbon tetrachloride is highly toxic and is environmentally unfriendly (Moyer et al. 2001). While 57 of the hazards had VP lower than cyclohexane, 9 had higher VP and require further study as empirical filtration performance data were not available and filtration performance data cannot be predicted for these chemicals. Chemicals with a VP higher than cyclohexane may be too volatile to be used as a TRA to evaluate the filtration of carbon-based canisters in the laboratory; these may be difficult to generate a reproducible challenge concentration and they would be weakly adsorbed to the carbon. Additionally, cyclohexane is an industry standard worldwide for evaluating OV filtration—e.g., for European and Japanese respiratory test requirements (Moyer et al. 2001; Furuse et al. 2001; HSE 2013; British Standards Institute (BSI) 1991). No TRAs were identified that were more appropriate or representative of the OV Family than cyclohexane.

Acid gas family

Of the 25 acid gases identified, 14 were ranked on the CTRA List as a fatality and/or public health risk (these hazards are not ranked by risk in this manuscript). Five of these 14 hazards are current NIOSH Acid Gas TRAs, and thus empirical filtration performance data is available. Five other hazards were considered unstable and not candidate TRAs for routine laboratory testing. Chlorine was one of four remaining candidate TRAs that were considered a high-risk hazard and was considered a candidate TRA. Therefore, chlorine was tested against 5 different commercial CBRN canister models for evaluation as a candidate TRA. The testing methodology and results for these commercial canisters will be described in detail in future publications; briefly, performance data showed chlorine was filtered effectively by all canisters tested and had a higher capacity (i.e., longer breakthrough time) in the carbon bed than 4 of NIOSH's current Acid Gas TRAs. Thus, NIOSH current TRAs offer more performance-limiting characteristics than chlorine.

Figure 4 shows an example of the carbon capacity for 11 acid gas chemicals when tested using a typical activated carbon under the same conditions. The asterisks show the 5 current NIOSH Acid Gas TRAs, representing performance-limiting chemicals in this family as well as phosgene that comprise unique filtration behavior. Multiple TRAs are necessary to cover the range of various interactions likely to occur within this family, including chemical adsorption, stoichiometric reaction, and catalytic removal. NIOSH's current TRAs represent relatively low performance in the carbon bed, making them suitable as a TRA for "worst case conditions." These acid gas TRAs were also chosen to represent chemical warfare agent classes: hydrogen cyanide and cyanogen chloride are blood agents that generally undergo weak physical adsorption and require copper, zinc, and TEDA

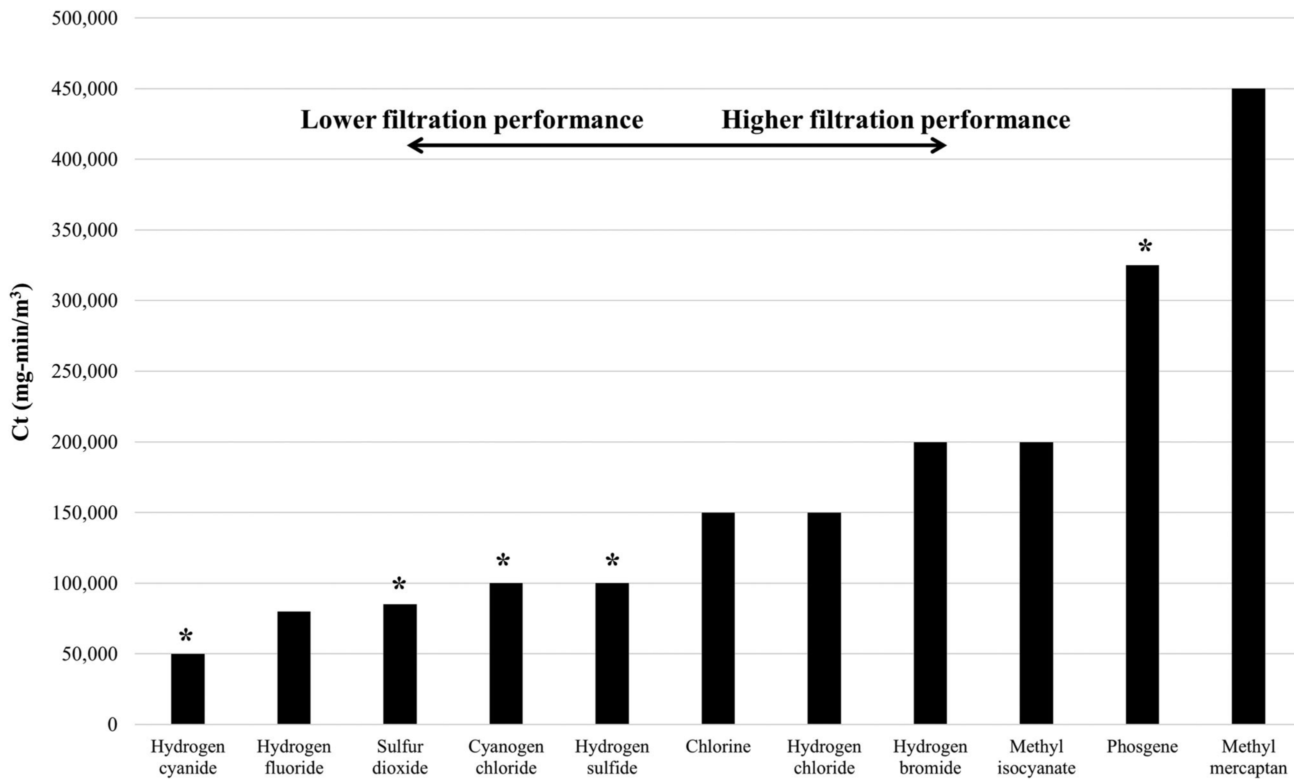

Figure 4. Breakthrough performance data for select acid gas-designated chemicals for a typical impregnated activated carbon used in commercial CBRN canisters (no pre-conditioning, tested at 15 %RH). Asterisks (*) represent current NIOSH TRAs.

impregnants, whereas phosgene is a choking agent and requires copper and zinc impregnants for effective filtration (Edgewood Chemical Biological Center (ECBC) 2001). Additionally, phosgene, hydrogen cyanide, and cyanogen chloride are used by the military to evaluate activated carbon performance (Edgewood Chemical Biological Center (ECBC) 2003). Hydrogen fluoride is not a candidate TRA due to its safety/handling issues in a laboratory setting (PennEHRS 2017). No TRAs were identified that were more appropriate/representative of the Acid Gas Family. NIOSH's current Acid Gas TRAs fit the "ideal TRA" characteristics—e.g., stable, able to produce appropriate challenge concentrations, available, and detectable.

Base gas family

Basic gases are removed primarily by physical adsorption, and secondarily through chemisorption. Therefore, the highest VP chemical in the family, represented by ammonia, serves as the suitable TRA for this family and the three other hazards identified.

Formaldehyde family

Formaldehyde exhibits self-polymerizing characteristics and is the only chemical that exhibits this behavior to a great extent within the activated carbon bed. The current TRA (formaldehyde) is the only chemical categorized into this family and thus remains the TRA.

Nitrogen oxides family

Nitrogen dioxide (NO_2) was grouped into its own family due to its unique ability to be readily reduced on the activated carbon bed and requiring a larger bed than those in the Acid Gas family (i.e., has a much lower capacity than acid gases). NO_2 serves as the TRA, however both nitric oxide (NO) and NO_2 are monitored during NIOSH approval testing.

Hydride family

Hydrides consist of arsine and phosphine, chemicals which have shown a unique ability to be readily oxidized on activated carbon filters by copper and silver impregnants (NIOSH 2018). As their removal chemistries have been reported to be similar, the highest VP chemical of the two, phosphine, has been regarded as the performance-limiting chemical for this family.

Particulate family

The primary criterion for this family is based on particle size. Particulate filter efficiency using DOP aerosol at the most penetrating particle size (0.2–0.3 µm) is an industry standard for evaluating HEPA/P100 filters (Stevens and Moyer 1989; NIOSH 2009; Vivid Air 2016). Thus, larger particles are not a suitable TRA and DOP remains the TRA for this family as opposed to the particulates identified in this assessment. Additionally, numerous studies and experimental data have historically shown that HEPA/P100 filters will adequately remove radiological particles with an efficiency of 99.97%.

Five hazards could not be categorized into NIOSH's Chemical Families based on the current NIOSH criteria for each family: (1) carbon monoxide; (2) propylene oxide; (3) ethyleneimine (aziridine); (4) propyleneimine; and (5) hydrogen selenide. These hazards could not be assigned to a current chemical family due either to physical/chemical properties outside the range of properties determined for each family, or their chemical properties or filtration properties were not well understood. These chemicals are expected to have limited capacity for physical adsorption due to their very high vapor pressures and may be filtered out by chemisorption with metal oxides. These chemicals require filter laboratory testing under various conditions to better understand whether they can be properly grouped into one of the existing chemical families. Carbon monoxide is generally not removed by activated carbon and requires chemisorption/chemical reaction mechanisms (Dey et al. 2017). Due to resources available within this study, laboratory testing has not yet been conducted for these five chemicals. If they can be grouped into an existing NIOSH Chemical Family, collecting empirical filtration data will determine if the existing TRA(s) are accurately representative. If any of the five chemicals cannot be grouped into current NIOSH Chemical Families, one or more additional Chemical Families may be needed.

One example of the four-step evaluation process is given for chlorosarin. Chlorosarin was identified as a hazard on the CTRA risk-based chemical assessment effort, and was included in the updated CBRN List as a candidate TRA. Chlorosarin was considered a gas/vapor in its natural state, and would be primarily filtered by physical adsoprtion based on its chemical and physical properties (e.g., lower VP). Because physical adsorption was considered to be the primary filtration mechanism based on its low VP, chlorosarin was categorized in the NIOSH OV Chemical Family. Chlorosarin was compared to the TRA for the OV Family—cyclohexane. The primary evaluation critera for OV chemicals is VP, and since chlorosarin has a lower VP than cyclohexane (i.e., 1.6 mmHg for chlorosarin at 25 °C and 100 mmHg at 25 °C for cyclohexane), cyclohexane will represent chlorosarin as the performance-limiting chemical in NIOSH's OV Chemical Family.

Discussion

A summary of the evaluation process used in this study for chemical and radiological hazards is shown in Figure 5. Many of the chemicals identified in the recent hazard assessments were TICs, which has been a recent emphasis for the protection of warfighters and emergency responders (Karwacki and Jones 2000; DeCoste and Peterson 2014). The increased use of TICs in industry results in an increased risk in accidental or intentional release (DeCoste and Peterson 2014).

The detailed process taken during the original 2001 evaluation of CBRN hazards was not published; however, some of the coauthors were key participants of this original evaluation and provided critical expertise to the current effort. Upon referring to FOUO/unpublished documentation, the process taken during the 2001 evaluation and the 2018 evaluation were similar: respiratory hazards were identified from multiple hazard assessment lists, were systematically evaluated based on selected criteria (e.g., VP, toxicity, filtration mechanisms), and TRAs were selected from the hazard assessment list based on their representativeness and performance-limiting characteristics within each Chemical Family (NIOSH 2018, Dietchman 2001). Because the NIOSH Chemical Families were not yet developed, the chemicals were originally categorized into "Strongly Physically Adsorbed", "Acids and Acid Gas Producers", "Bases and Base Gas Producers", "Cyanides/Cyanates", "Chloroformates", "Hydrides", "Aldehydes/Ketones", "Sulfides", "Boranes", "Silanes/Silicates", "Nitrogen Oxides", "Metal Carbonyls", "Marginally Physically Adsorbed/No Apparent Reactive Mechanism", "Poorly Physical Adsorbed/No Known Practical Removal Mechanism", and "Poorly Physically Adsorbed/Further Study Required". These categories were further refined into NIOSH's current seven Chemical Families. In the current evaluation, the seven Chemical Families were still deemed appropriate. A key difference between the 2001 and the current evaluation is the availability of recent chemical hazard assessments conducted by DHS and empirical filtration performance data to assist with groupings into each Chemical Family. Grouping chemicals by functional groups and other similar chemical/physical properties is commonly done to evaluate filtration

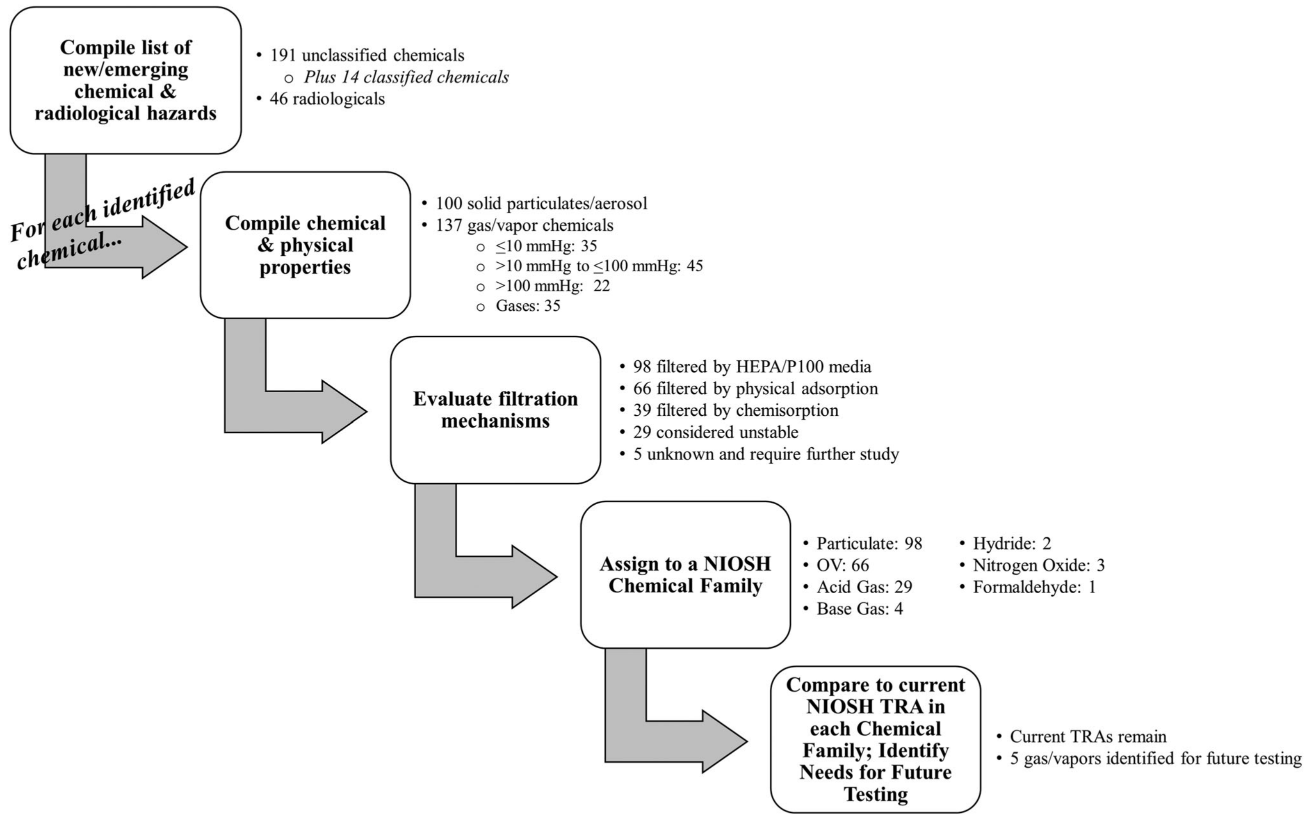

Figure 5. Overall summary of the CBRN hazards evaluation process and results.

performance (DeCoste and Peterson 2014, Dietchman 2001, Karwacki and Jones 2000).

Much effort was placed on compiling chemical/physical properties that were ultimately not used in Steps 3 and 4. For example, liquid density, relative vapor density, diffusivity in air, solubility in water, NIOSH recommended exposure limits, and NFPA health/flammability/reactivity scores were compiled but not ultimately used during the evaluation.

A limitation of this study was that the evaluation does not include the analysis of breakthrough products that may be generated during the chemisorption reaction with impregnants. With considerations to resources, a comprehensive chemical analysis for every hazard could not be identified. Therefore, it was not feasible to collect empirical filtration data for all chemicals where data was unavailable, and thus assumptions were made based on similar chemicals' properties and researchers' professional judgment. Unlike OV where filtration is primarily based on VP, it is challenging to speculate the filtration mechanisms for reactive gases that require chemisorption (e.g., acid gases). Potential future work includes testing all chemicals identified for filtration performance data with measured breakthrough data. Testing radiological particulates is not necessary since numerous studies and experimental data has historically shown that HEPA/P100 filters will adequately remove radiological particles; radiological gas/vapors removal is increased by the activated carbon being impregnated with 2% triethylenediamine, which is common for both military and commercial CBRN canisters (TEDA; Ho et al. 2019).

The general criteria and steps used during this evaluation process may be used by other entities, including manufacturers or industry standard-setting bodies (e.g., European standard EN 141 (CEN 2000)), that choose to select representative chemicals from a list of hazards for testing of activated carbon-based respirator technologies. As new hazards emerge, threat assessments should be continually reviewed, and respirator performance standards should continue to be developed or modified as needed to ensure current respirator technologies provide adequate protection to emergency responders.

Conclusion

NIOSH, DOD, and DHS reviewed chemical and radiological hazard assessments and conducted a four-step evaluation process to ensure NIOSH-approved CBRN APR canisters protection capabilities would continue to provide adequate protection against exposure to newly identified chemicals, and to determine if a change to the current NIOSH TRAs or Chemical Families was necessary. A list of 237 CBRN hazards was compiled and theoretically evaluated against the current NIOSH TRA in the respective NIOSH Chemical Family. To specifically evaluate each candidate TRA, an evaluation process was developed. Sixty-six chemicals were characterized into NIOSH's Organic Vapor Family, 27 into the Acid Gas Family, 4 into the Base Gas Family, 1 in the Formaldehyde Family, 3 into the Nitrogen Oxides Family, 2 in the Hydride Family, and 102 into the Particulate Family (i.e., 56 chemical and 44 radiologicals). Twenty-nine chemicals were considered to be unstable and were excluded as candidate TRAs. Five chemicals were identified as requiring further study.

Five chemicals identified as part of this hazard assessment require further evaluation to confirm that current respiratory technology provides adequate protection. Those chemicals are currently being tested with NIOSH-approved CBRN APR system canisters. Collecting this empirical data is important so manufacturers are better informed of the potential need for design modifications, and so emergency responders are aware of their respiratory protection limitations. It was determined that the current NIOSH TRAs adequately represent all chemical and radiological hazards identified in this recent hazard assessment and no changes are needed at this time. This evaluation process can be used for future hazard assessments, which can be conducted on a routine basis. NIOSH will update its respiratory guidance for emergency responders to include these recently identified hazards.

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Disclaimer

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention.

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